

The mother liquors from the crystallization of the *o*-acid were evaporated to dryness and attempts were made to separate the components by fractional crystallization. Only a small quantity (0.22 g.) of the pure *m*-isomer was obtained, m. p. 103–104.5° (lit.¹⁸ m. p. 103°), which was identified by conversion to isophthalic acid (methyl ester, m. p. 62–63°). The balance of the solid crystallization residues (4.1 g.) was analyzed by hydrolysis with hot 80% sulfuric acid and separation of the resulting phthalic acids by the method of Smith.¹⁹ From 1.08 g. of the crystallization residue there was obtained 0.36 g. (33%) of phthalic acid, 0.56 g. (48%) of isophthalic acid and 0.02 g. (2%) of terephthalic acid. On this basis the composition of the original mixture of trifluoromethylbenzoic acids was *ortho*, 83%; *meta*, 16%; and *para*, <1%.

Competitive Metalation Reaction. Anisole and Benzotrifluoride.—To an ethereal solution of *n*-butyllithium (0.1

mole) was added rapidly a mixture of anisole (10.8 g., 0.1 mole) and benzotrifluoride (14.8 g., 0.1 mole). The resulting mixture was refluxed for two hours and then carbonated. After the non-acidic materials had been extracted with ether, acidification gave 6.0 g. (40%) of crude acid, m. p. 90–98°. The product was recrystallized from benzene-petroleum ether giving 5.9 g. of pure *o*-anisic acid, m. p. 100–102° (mixed melting points with *o*- and *m*-trifluoromethylbenzoic acids <85°).

Summary

Benzotrifluoride is metalated by *n*-butyllithium less readily than anisole but more readily than benzene. Carbonation of the metalation products of benzotrifluoride gives *o*- and *m*-trifluoromethylbenzoic acids in a ratio of about five to one.

CAMBRIDGE 38, MASS.

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(18) Swarts, *J. chim. phys.*, **17**, 32 (1919).

(19) Smith, *THIS JOURNAL*, **43**, 1920 (1921).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DAVIDSON COLLEGE]

The Effect of KCl, NaCl and Na₂SO₄ on the Aqueous Solubility of Acetanilide

BY THOMAS S. LOGAN

Because of its rather low solubility in water, and the convenience and accuracy with which this solubility can be determined,¹ acetanilide is particularly well suited for the study of salting out phenomena. The desirability of comprehensive studies in this field has been pointed out by various investigators.² This paper reports measurements of the solubility of acetanilide in solutions of potassium chloride, sodium chloride and sodium sulfate at ionic strengths from 0.05 to 4 and at temperatures from 0 to 60°.

Experimental

The solubility of acetanilide was determined by the method previously described.¹ The potassium chloride, sodium chloride and sodium sulfate used in making up the solutions were C. P. salts. They were dried at 130° from two to three hours before use. Check experiments showed that their presence in solution had no effect on the determination of acetanilide.

A solution was prepared by putting into a dry solubility flask a weighed portion of salt. To this was added acetanilide in excess of that necessary for saturation. The flask was closed with a rubber stopper and weighed. Approximately the required quantity of hot water was then pipetted into the flask. It was stoppered and weighed again. The flask was shaken as it cooled. At a few degrees above the temperature of the determination the stopper was quickly removed and replaced by a stopper containing the tubes for withdrawing the solution. The flask was then put into the thermostat. A few experiments were run where equilibrium was approached from the low temperature side. The results were concordant with the others. Two samples of the solution were withdrawn for acetanilide analysis. These duplicate analyses showed an averaged error of ±0.16% from their means. An error of ±0.5%, or more, was obtained in 5% of the analyses. The largest error was ±0.6%.

(1) Logan, *THIS JOURNAL*, **67**, 1182 (1945).

(2) (a) Glasstone and Pound, *J. Chem. Soc.*, **127**, 2660 (1925); (b) P. M. Gross, *Chem. Rev.*, **13**, 91 (1933); (c) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., p. 400; (d) Akerlof, *THIS JOURNAL*, **57**, 1196 (1935).

The concentrations of the salt solutions reported are those secured by direct weighing, as described above. As a check, a number of chloride analyses were run on solution samples withdrawn from the flasks. These were taken at the same time that samples for acetanilide analysis were withdrawn. The results gave an average error of ±0.5% in comparison with the listed values of the ionic strength. The estimated maximum error in solubility resulting from this deviation in ionic strength is shown in Table I.

TABLE I

Ionic strength	Error, ±%
1, or less	0.2
2, or less	.5
3, or less	.7
4, or less	.9

Weight corrections to vacuum were applied where appropriate. For the salt solutions the densities were taken as those listed in the "International Critical Tables" for the salt solutions in water.

The thermostat was regulated to ±0.05° at temperatures of 40° and lower. The regulation was ±0.10 at the two higher temperatures. The estimated effect of this variation on the solubility was ±0.2% at the lower and ±0.4% at the higher temperatures.

Results

The results have been evaluated on a basis of the Randall and Failey modification³ of the well-known Setschenow equation

$$\log S_0/S = k\mu$$

where S_0 and S are the solubilities of the acetanilide in pure water and the salt solution, respectively, μ is the ionic strength, and k is the salting out constant.

Table II records the solubility, S_0 , of acetanilide in pure water at the temperatures studied. S_0 is given as grams of acetanilide per 100 g. of water. Except for the values at 15 and 32.6°, these data were calculated from those of the

(3) Randall and Failey, *Chem. Rev.*, **4**, 271 (1927).

TABLE II

Temp., °C.	S_0	k		
		KCl	NaCl	Na ₂ SO ₄
0	0.361	0.149	0.173	
15	.501	.141	.166	0.191
25	.643	.145	.165	.194
30	.734	.141	.165	
32.6	.789			.185
40	.983	.142	.164	
50	1.34	.146	.164	.183
60	1.89	.146	.166	

earlier paper.¹ Also shown are the values of k , the salting out constants for the three salts at the various temperatures, obtained from plots of $\log S_0/S$ versus μ .

Figures 1, 2 and 3 show plots of the difference, $\log S_0/S - k\mu$, versus μ . The circles are drawn with a diameter of 0.003 on the ordinate scale. Values of the difference, $\log S_0/S - k\mu$, taken

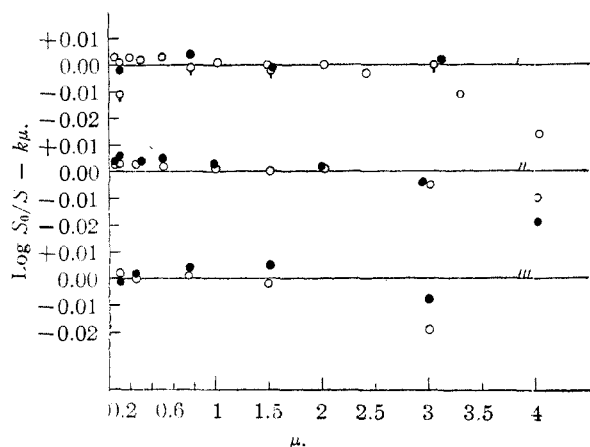


Fig. 1.—Salt, KCl: I, ○—0°; ●—15°; ○—25°; II, ○—30°; ●—40°; III, ○—50°; ●—60°.

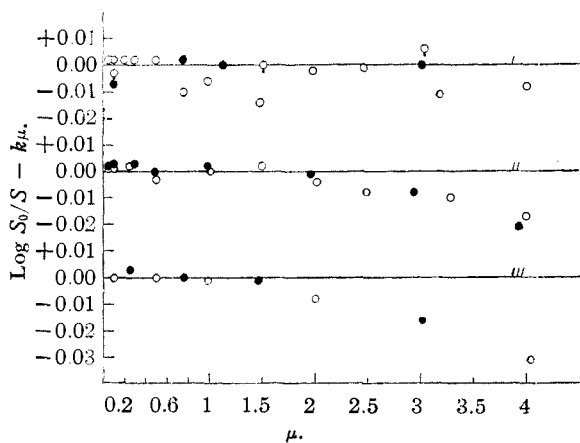


Fig. 2.—Salt, NaCl: I, ○—0°; ●—15°; ○—25°; II, ○—30°; ●—40°; III, ○—50°; ●—60°.

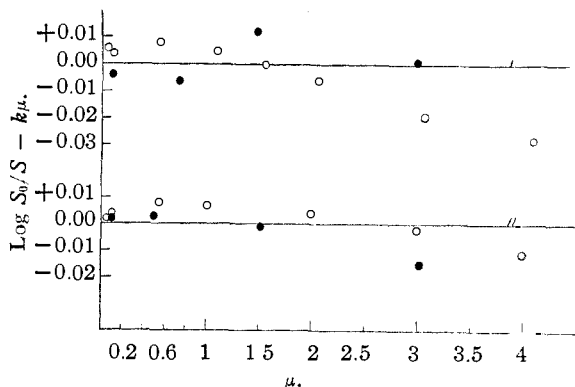


Fig. 3.—Salt, Na₂SO₄: I, ●—15°; ○—25°; II, ○—32.6°; ●—50°.

from these plots, can be combined with the data of Table II to reproduce the experimental results with an error of ± 1 in the third significant figure. The values of S calculated in this way will express grams of acetanilide per 100 g. of water. The errors of determination mentioned in the experimental section have been combined in Table III to show the maximum mean-square error of the experimental results.

TABLE III

μ	Error, %	
	0-40°	50-60°
1, or less	0.3	0.5
2, or less	.6	.7
3, or less	.8	.8
4, or less	.9	1.0

Randall and Failey,³ in their studies of the salting out effect, have mentioned that the salting out constant, k , probably varies with temperature, the values tending to be higher at the lower temperature. Goeller and Osol⁴ have studied the salting out of molecular benzoic acid at 35°, and have compared their constants with those of other investigators. They state that their results indicate that there is no significant change in k over the temperature range 18 to 35°. The findings of this paper, over a more extended range of temperature, would seem to be in accord with those of Goeller and Osol.

This work is being continued.

Summary

The solubility of acetanilide in solutions of potassium chloride, sodium chloride and sodium sulfate over an extended range of temperature and concentration has been measured.

DAVIDSON, NORTH CAROLINA

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(4) Goeller and Osol, THIS JOURNAL, 59, 2132 (1937).